

# THE RELATION BETWEEN TAR AND EXTRACTABLES FORMATION AND CROSSLINKING DURING COAL PYROLYSIS

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## ABSTRACT

This paper presents a combined study of tar and extractables formation and crosslinking processes during rapid pyrolysis of coal. Tar and extractables were characterized by gel permeation chromatography, and crosslinking by a solvent swelling technique. The behaviors of coals ranging in rank from low volatile bituminous to a lignite were examined. It was noted that the low rank coal crosslinks at a much lower temperature than the high volatile bituminous coals, and that the low volatile bituminous coal is already highly crosslinked to begin with. These observations may help explain the widely differing yields and nature of tars and extractables produced by pyrolysis of these different ranks of coal.

## INTRODUCTION

It has recently been shown that the technique of solvent swelling, as has been applied to the analysis of the macromolecular structure of coals<sup>1</sup>, can also be applied to the analysis of chars produced by pyrolysis<sup>2</sup>. This technique is utilized in this paper to help shed further light on the complex processes of "depolymerization" and charification that occur during pyrolysis of coals. In particular, the differences manifested by coals of different ranks are considered.

## EXPERIMENTAL

The analyses of the four coals examined in this study are provided in Table 1. All samples used in this study had particles in the size range 53-88  $\mu$ m. Pyrolysis was performed in an electrically heated wire mesh, which assures uniform and rapid heating of all particles. All experiments were performed with a heating rate of roughly 1000 K/s, up to the indicated peak temperature, followed by cooling at a rate between 200 and 400 K/s. All pyrolyses were performed either in vacuum or in atmospheric pressure helium.

Table 1  
Ultimate Analyses of Coals Examined\*

	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Ash</u>	<u>Mois- ture</u>
Bruceton Pitts, No. 8 bituminous	80.4	5.3	6.7	1.6	1.0	4.6	1.7
Hillsboro Ill. No. 6 bituminous	67.2	4.6	12.3	1.2	3.4	11.7	8.6
W. Va. Pocahontas low volatile bit.	84.4	4.2	3.7	0.3	0.5	6.8	0.2
Beulah, No. Dakota Lignite	66.7	3.7	19.5	0.9	0.8	9.3	32.4

\*All results on a dry basis except moisture, which is reported on an as-received basis. All analyses by Huffman Laboratories, Inc.

As used in this paper, the term "tars" refers to room temperature condensable products which have been expelled from the particles during pyrolysis. These materials generally have a molecular weight greater than 100, and are more than 97% soluble in tetrahydrofuran (THF). Extractables are materials left behind in the char, which are THF soluble. The extraction procedure is very mild,

involving a 1-hour ultrasonicated soak in THF (during which time the THF reached reflux temperatures). The sum of tar plus extractables is referred to as metaplast--the softened, transportable fraction of the coal. It is important to bear in mind that the estimate of metaplast obtained by summing tar plus extractables is a minimum value for that present in the coal during actual pyrolysis, since some recombination reactions may occur between extractables and unextractable char during cooling.

The analysis of the molecular weight distributions of the tars and extractables is performed by gel permeation chromatography (GPC), as has been described elsewhere<sup>3</sup>. It should be noted that calibration of the GPC columns was performed by vapor phase osmometric measurement of the molecular weights of actual fractionated samples of Bruceton coal tars.

The solvent swelling technique has also been described elsewhere<sup>1,2</sup>. It involves measurement of the height of columns of coals and chars immersed in pyridine, in order to determine volumetric swelling ratios in the presence of the solvent. With a knowledge of the nature of solvent-coal interaction, this information can be used to estimate molecular weight between crosslinks in the coals and chars.

## RESULTS AND DISCUSSION

In an earlier communication, it was shown that the Bruceton bituminous coal apparently crosslinks at a somewhat higher temperature than does the North Dakota lignite<sup>2</sup>. This is consistent with the viewpoint that early crosslinking prevents softening of low rank coals during pyrolysis. This observation is also consistent with the low tar formation tendency of low rank coals, in the sense that tar precursors are quickly crosslinked into the char of low rank coals, prior to their escape.

The solvent swelling tendency of the coal chars has been used as a qualitative index of the extent of crosslinking; the higher the swelling ratio, the lower the degree of crosslinking. In this manner, comparative solvent swelling data are shown for all four ranks of coal, in Figure 1.

The low volatile bituminous coal swells to an extent of less than 5% in both the unpyrolyzed state and as a char. Consequently, it is difficult to say much about changes in the network structure of this coal during pyrolysis, based on solvent swelling information.

The Illinois #6 high volatile bituminous coal has swelling behavior very similar to that observed for the Bruceton high volatile bituminous coals. Both these coals soften markedly and both yield copious amounts of tar during pyrolysis. As noted previously<sup>2</sup>, both these coals show little further tar formation at temperatures above about 900 K, a temperature at which new crosslink formation is quite measurable by this technique. It may be noted that the tars of these coals also show remarkably similar molecular weight distributions<sup>1</sup>.

In contrast, little tar formation is seen at temperatures much in excess of 700 K in the case of the North Dakota lignite<sup>2</sup>. On the basis of the high volatile bituminous and lignite data it might be tempting to ascribe significance to a swelling ratio of about 2 as the lowest value at which tar formation is possible. This of course is inappropriate, since the low volatile Pocahontas coal yields significantly more tar than the lignite, despite its highly crosslinked nature. Table 2 shows the yields of tar from the Pocahontas sample.

Table 2  
Pocahontas Tar Yields

<u>Temperature (K)</u>	<u>Yield (wt. %, as received)</u>	<u>MW<sub>N</sub></u>
737	3.0	244
1083	9.1	199

The number average molecular weight of the Pocahontas tar is seen to significantly decline with increasing temperature. The actual molecular weight distributions are seen in Figure 2. The molecular weight distributions shown in Figure 2 (and later in Figure 3) are partially integrated molecular weight distributions. The ordinate represents the weight percent of tar at any molecular weight  $\pm 100$  mass units of the abscissa value.

The sharp peak of the Pocahontas tar molecular weight distribution in the range 300-500 is quite different than that of the tars of lower rank bituminous coals; as shown previously, these coals have a peak in the range from 600 to 700<sup>3</sup>. The implication appears to be that the Pocahontas coal is as highly crosslinked to start, that it is unlikely that enough bonds can break so as to yield large tar fragments. Or, viewed another way, the larger the fragment of coal to be released by bond breakage processes, and the higher the crosslink density, the lower the probability that enough bonds can be broken during pyrolysis in order to release the fragment.

Figure 3 shows the variation of molecular weight distribution with temperature for the North Dakota lignite. The number average molecular weight at 737 K is 323, whereas at 1133 K it is 279. The decrease in number average molecular weight of the tar species with increasing temperature in the case of the lignite (and the low volatile bituminous coal) is contrary to what might be expected based on vapor pressure arguments (higher temperatures should promote vaporization of even larger fragments of the coal). This trend towards lower number average molecular weight of fragments with increasing severity of thermal treatment is, however, consistent with the data that imply a higher degree of crosslinking with a more severe thermal treatment. It has been shown that in a polycondensation process, the molecular weight of extractables decreases with extent of polycondensation<sup>4</sup>. This behavior is not observed in the case of the high volatile bituminous coals, which show little variation of either number average molecular weight or molecular weight distributions with increasing temperature<sup>3</sup>. Presumably this reflects the fact that little crosslinking occurs during the active tar formation period<sup>2</sup>.

The molecular weight distributions of the extracts of the Bruceton high volatile bituminous coal have been shown previously<sup>3</sup>. These data are summarized in Table 3, along with data on the metaplast (sum of tar plus extractables) molecular weight distribution for this same coal.

Table 3  
Molecular Weight Distributions of Extractables and Metaplast  
from Bruceton Bituminous Coal\*

<u>Molecular Weight Range</u>	<u>Extractables</u>	<u>Metaplast</u>
100-1100	17% wt.	46% wt.
1100-2100	31%	31%
2100-3100	24%	13%
3100-4100	13%	5%
>4100	15%	5%
NO. AVG. MOL. WT.	1002	533

\*All results for vacuum pyrolysis to a peak temperature of roughly 740K.

The difference between the extractables and metaplast arises from the fact that the latter contains a substantial contribution of species which were sufficiently light so as to have evaporated and been measured as tar, outside the particle.

A comparison of the number average molecular weight of the extractable pyrolysis fragments and the number average molecular weight between crosslinks is useful in characterizing the manner in which the crosslinked structure breaks down. In order to calculate the molecular weight between crosslinks from solvent swelling data, the Flory-Rehner equation is often employed<sup>2</sup>, but is subject to criticism when applied to highly crosslinked, rigid networks<sup>6,7</sup>. Nevertheless, the Flory-Rehner equation is often used as an approximation because of the lack of information concerning the repeat unit size, needed for more sophisticated models<sup>8,9</sup>. The Flory-Rehner equation may be expressed as:

$$\bar{M}_c = - \frac{\rho_c M_s}{\rho_s} \frac{\phi^{1/3}}{\ln(1-\phi) + \phi + X\phi^2}$$

where  $\rho_c$  is the density of the original coal,  $\rho_s$  is the density of the solvent,  $M_s$  is the molecular weight of the solvent,  $X$  is the solvent-network interaction parameter, and  $\phi$  is the inverse of the swelling ratio. The evaluation of  $X$  is also difficult, particularly since pyridine is a specifically interacting solvent. Table 4 shows a range of  $X$  values and their effect on  $\bar{M}_c$  for the Bruceton coal (or char up to about 800 K).

Table 4  
Typical Values of  $\bar{M}_c$  for Bruceton Coal

$X$	$\bar{M}_c$
0.3	1105
0.4	1464
0.5	2172
0.6	4204

The range of  $\bar{M}_c$  obtained by this method compares well with estimates based on a rigid chain model applied to comparable ranks of coal<sup>9</sup>, in the range  $x = 0.3$  to  $0.5$ . It is seen that the extractable and transportable fragments of the coal have a number average molecular weight which is comparable to or smaller than the number average molecular weight between crosslinks, for any reasonable value of  $X$ .

#### CONCLUSIONS

1. A lignite is seen to crosslink at much lower pyrolysis temperatures than high volatile bituminous coals. A low volatile bituminous coal is already too highly crosslinked to use solvent swelling to track pyrolysis behavior.
2. The downward shift in molecular weight distributions of pyrolysis tars with increasing temperature from a lignite and a low volatile bituminous coal is consistent with occurrence of polycondensation during pyrolysis.
3. Pyrolysis fragments appear to be, on average, comparable in size to or smaller than the number average molecular weight between crosslinks in a Bruceton bituminous coal.

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# REFERENCES

1. Green, T. K., Kovac, J. and Larsen, J. W., *Fuel*, **63**, 935 (1984) and references cited therein.
2. Suuberg, E. M., Lee, D. and Larsen, J. W., "Temperature Dependence of Crosslinking Processes in Pyrolyzing Coals", accepted for publication in *Fuel*.
3. Unger, P. E. and Suuberg, E. M. *Fuel*, **63**, 606 (1984).
4. Van Krevelen, D. W., *Fuel*, **44**, 229 (1965).
5. Flory, P. J. and Rehner, J., *J. Chem. Phys.*, **11**, 521 (1943).
6. Larsen, J. W. and Kovac, J., *Am. Chem. Soc. Symp. Series No. 71*, J. Larsen, Ed., 36 (1978).
7. Lucht, L. M. and Peppas, N. A., *Am. Chem. Soc. Symp. Series No. 169*, B. Blaustein, B. Bockrath, and S. Friedman, Eds., 43 (1981).
8. Kovac, J., *Macromolecules*, **11**, 362 (1978).
9. Peppas, N., Lucht, L., Hill-Lievens, M., and Hooker, A., D.O.E. Final Technical Report DE-FG22-80PC30222, U. D. Department of Energy, August 1983.

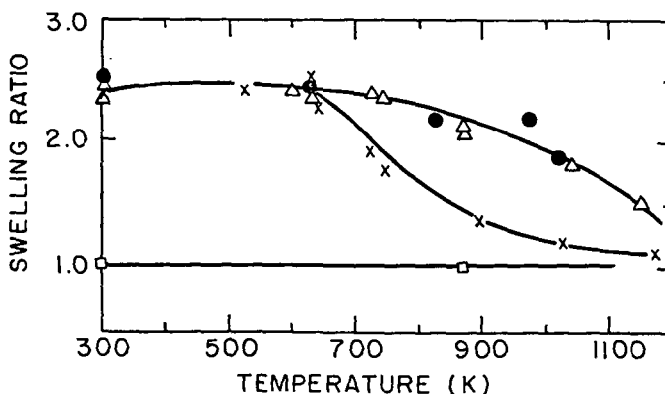


Figure 1. Pyridine swelling ratio as a function of peak pyrolysis temperature for four coals. (●) Illinois No. 6, (Δ) Bruceton, (X) Beulah Lignite, (□) Pocahontas.

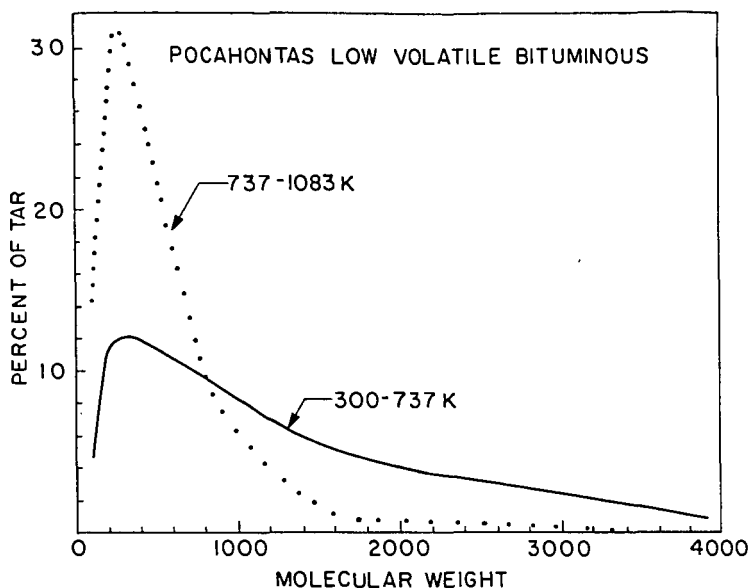


Figure 2 (top). Molecular weight distribution of tars evolved during pyrolysis of Pocahontas low volatile bituminous coal. Curves show range of pyrolysis temperatures over which the tar was evolved. Partially integrated curves, as described in text.

Figure 3 (bottom). Molecular weight distribution of tars evolved during pyrolysis of Beulah lignite. Curves show range of pyrolysis temperatures over which the tar was evolved. Partially integrated curves.

